

Preliminary communication

A novel porphyrin-ferrocene-quinone linked molecule

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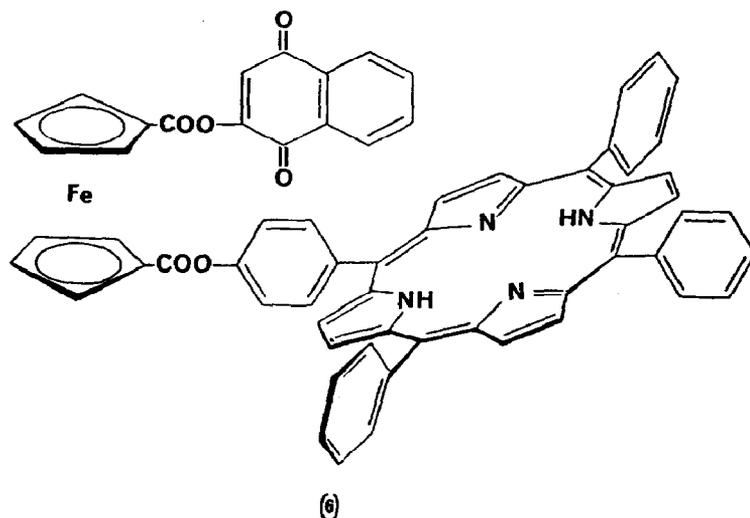
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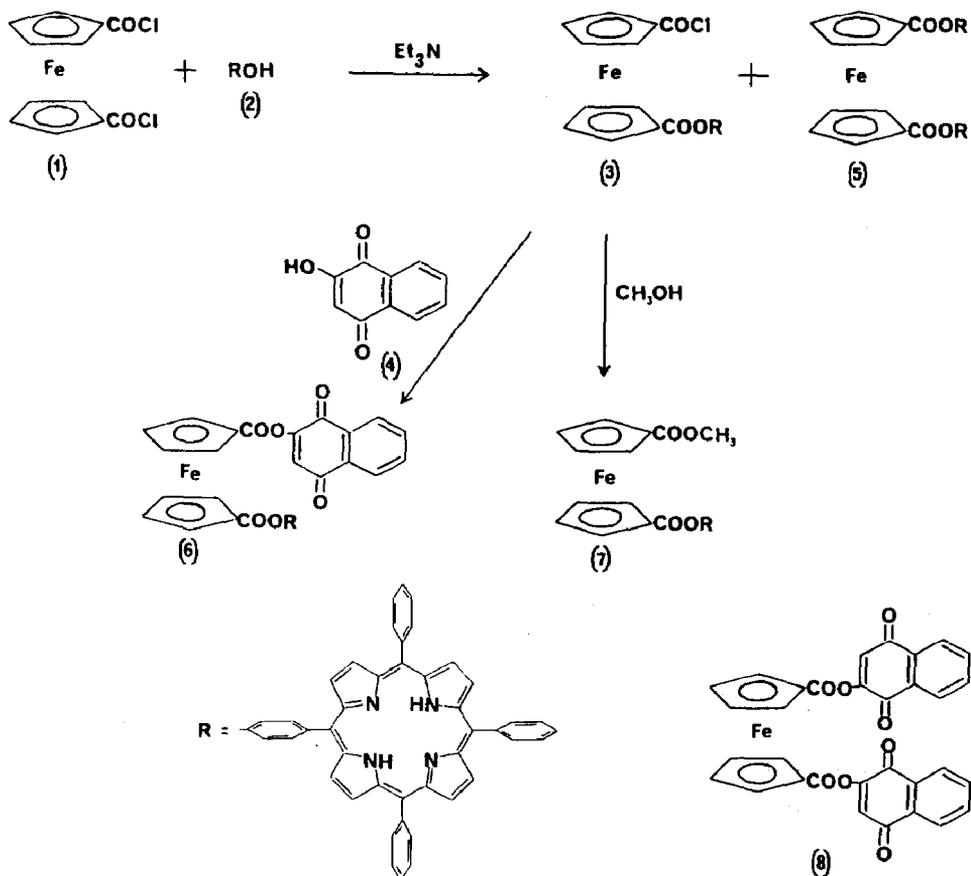
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Abstract

The synthesis and electrochemistry are reported of a new porphyrin-ferrocene-quinone linked molecule (**6**) prepared in a stepwise procedure from 1,1'-bis(chloro-carbonyl)ferrocene (**1**), 5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphyrin (**2**), and 2-hydroxynaphthoquinone (**3**).

Because of the key role porphyrin pigments play in photophysical and redox processes in nature, such as bacterial photosynthetic reactions [1,2] the design and synthesis of abiotic porphyrin macrocycles continue to attract considerable attention [3-7]. As part of a programme concerned with the construction of macrocycles containing multiple redox-active centres [8,9] including porphyrins [10], which may





serve as new types of electron relay catalysts for redox and photochemical reactions, we report here the synthesis and electrochemistry of a novel porphyrin-ferrocene-quinone linked molecule **6**. The preparation of **6** was achieved in a simple 'one pot' stepwise procedure. The condensation of 1,1'-bis(chlorocarbonyl)ferrocene (**1**) [11] with one molar equivalent of 5-(*p*-hydroxyphenyl)-10,15,20-triphenylporphyrin (**2**) [12] in the presence of triethylamine in dry refluxing toluene gave the monosubstituted ferrocene-porphyrin intermediate (**3**) in situ. Addition of one molar equivalent of 2-hydroxynaphthoquinone (**4**) to the toluene solution of **3** followed by column chromatographic separation (silica, eluent CH₂Cl₂) gave two major fractions. The first was the ferrocene bis-porphyrin (**5**) [10] and the second the desired compound **6** in 35% yield, not optimised. Its structure was characterised by elemental analysis [13], mass spectrometry, and ¹H NMR spectroscopy [13]. Analogous synthetic routes were used to prepare the ferrocene porphyrin (**7**) and the ferrocene bisquinone (**8**).

Cyclic voltammetry and differential pulse voltammetry were used to study the redox chemistry of **5**, **6**, **7** and **8**, and the results and assignment of $E_{1/2}$ values are presented in Table 1. It is noteworthy that the respective separations between the first porphyrin oxidation and first porphyrin reduction potential agree well with the

Table 1

Electrochemical data; $E_{1/2}$ values (V)^a

Compound	Ferrocene oxidation	Porphyrin ring oxidation		Porphyrin ring reduction		Quinone reduction	
5	+1.12	+1.36 ^b	+1.12 ^b	-1.09 ^b	-1.41 ^b	-	-
6	+1.14	+1.37	+1.14	-1.07	-1.41	-0.47	-0.99
7	+1.08	+1.32	+1.08	-1.07	-1.41	-	-
8	+1.16	-	-	-	-	-0.47 ^b	-1.21 ^b

^a Obtained from cyclic voltammetry studies in dichloromethane solvent containing 0.2 M $[\text{Bu}_4\text{N}]\text{BF}_4$ as supporting electrolyte. Solutions were ca. 2×10^{-3} M and measurements made at $21 \pm 1^\circ \text{C}$ at 0.2 V s^{-1} scan rate using a Pt bead working electrode with ferrocene internal reference. Values are quoted relative to the saturated calomel reference electrode. ^b Two electron process.

“theoretical” difference of $2.25 \pm 0.15 \text{ V}$ observed for radical-anion and radical-cation formation [14].

Fluorescence measurements (1×10^{-5} M solutions in dichloromethane, excitation at 510 nm) were carried out on **6** and 90% fluorescence quenching of the porphyrin chromophore (versus tetraphenyl porphyrin reference) was observed. This result suggests that rapid electron transfer takes place from the singlet excited state of the porphyrin to the quinone acceptor.

The possibility that **6** may act as a new type of electron relay catalyst in redox reactions is under investigation.

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References

- 1 J. Deisenhofer, O. Epp, K. Miki, R. Huber and H. Michel, *J. Mol. Biol.*, 180 (1984) 3852.
- 2 P. Allen, G. Feher, T.O. Yeates, H. Komiya and D.C. Rees, *Proc. Natl. Acad. Sci. U.S.A.*, 84 (1987) 5730.
- 3 D. Gust, T.A. Moore, L.R. Makings, P.A. Liddell, G.A. Nemeth and A.L. Moore, *J. Am. Chem. Soc.*, 108 (1986) 8028.
- 4 J.A. Cowan, J.K.M. Sanders, G.S. Beddard and R.J. Harrison, *J. Chem. Soc. Chem. Commun.*, (1987) 55.
- 5 E.S. Schmidt, T.S. Calderwood and T.C. Bruice, *Inorg. Chem.*, 25 (1986) 3718.
- 6 J.L. Sessler and M.R. Johnson, *Angew. Chem. Int. Ed. Engl.*, 26 (1987) 678.
- 7 J. Davila, A. Harriman, M.C. Richoux and L.R. Milgrom, *J. Chem. Soc. Chem. Commun.* (1987) 525.
- 8 P.D. Beer and E.L. Tite, *Tetrahedron Lett.*, 29 (1988) 2349.
- 9 P.D. Beer, M.G.B. Drew, A. Ibbotson and E.L. Tite, *J. Chem. Soc. Chem. Commun.*, (1988) 1498.
- 10 P.D. Beer and S.S. Kurek, *J. Organomet. Chem.* 336 (1987) C17.
- 11 H.J. Lorkowski, R. Pannier and A. Wende, *J. Prakt. Chem.*, 35 (1967) 149.
- 12 L.R. Milgrom, *J. Chem. Soc. Perkin Trans I*, (1983) 2535.
- 13 ¹H NMR (CDCl_3) for **6**; -2.81 (2H, s), 4.78 (2H, t, J 1.8 Hz), 4.89 (2H, t, J 1.8 Hz), 5.17 (2H, t, J 1.8 Hz), 5.34 (2H, t, J 1.8 Hz), 6.93 (1H, s), 7.61 (2H, d, J 8.4 Hz), 7.72–7.77 (11H, m), 8.06 (2H, m), 8.14 (2H, m), 8.22 (22H, m), 8.85 (8H, s) $\text{C}_{66}\text{H}_{42}\text{FeN}_4\text{O}_6$ requires C, 75.9, H, 4.2, N, 5.4 found C, 76.1, H, 4.2, N, 5.5.
- 14 K.M. Kadish, *Prog. Inorg. Chem.* 34 (1986) 435.